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CHLORINATIVE CLEAVAGE OF PERMETHYLPOLYSILANES INITIATED BY PHOTO-INDUCED ELECTRON TRANSFER[1]

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Irradiation of dodecamethylcyclohexasilane (**1**) in CCl_4-CH_2Cl_2 in the presence of 9,10-dicyanoanthracene (**2**) afforded 1,6-dichlorododecamethylhexasilane in 70% yield. Fluorescence of 2 was quenched by 1 with a diffusion-controlled rate. A mechanism of free-radical chlorination involving $(\mathbf{1})^{+\cdot}$ is proposed.

In a previous paper,[2] we have reported the first clear example of electron-transfer induced photochemical reaction of silicon-silicon bonded species in the presence of electron acceptor. Namely, the reaction of dibenzodisilacyclohexadiene with tetracyanoethylene under illumination with a sodium lamp gave a silylene-extrusion product by an electron-transfer mechanism. We have also reported that permethylpolysilanes form charge-transfer complexes with tetracyanoethylene in dichloromethane.[3] In this paper, we describe chlorinative cleavage of the silicon-silicon bonds of permethylpolysilanes initiated by photo-induced electron transfer.

Irradiation of dodecamethylcyclohexasilane (**1**, λ_{max} 255 nm, ε 2000) in a mixed solvent of carbon tetrachloride and dichloromethane in the presence of 9,10-dicyanoanthracene (DCA, **2**) resulted in the formation of 1,6-dichlorohexasilane (**3**) and hexachloroethane (**4**). The latter was detected by GC-MS. (Table 1)

$$\underset{\mathbf{1}}{(Me_2Si)_6} \xrightarrow[DCA/CCl_4-CH_2Cl_2]{h\nu\ (\lambda>300\ nm)} \underset{\mathbf{3}}{Cl-(SiMe_2)_6-Cl} + \underset{\mathbf{4}}{Cl_3C-CCl_3}$$

The reaction did not occur without DCA under the conditions and it is clear that DCA should be excited first by light of wavelength longer than 300 nm. Furthermore, ΔG value calculated by the Rehm-Weller equation[4,5] is -17 kcal/mol, indicative of exothermic electron-transfer from the polysilane to the excited singlet state of DCA. In order to confirm this, we then carried out the quenching experiment of the fluorescence of DCA in dichloromethane.

A dichloromethane solution of DCA was excited at 400 nm and the emission band (410-560 nm, λ_{max} = 434 nm) was quenched with **1** (0.153-5.05×10^{-3} M) to yield a good linear Stern-Volmer plot with $k_q\tau = 456\pm25\ M^{-1}$ (r = 0.986). From the literature value of τ (11.7 ns)[7] for DCA, k_q is calculated to be $3.90\pm0.21\times10^{10}\ M^{-1}s^{-1}$. Namely, fluorescence of DCA was quenched with a diffusion-controlled rate.

Linear permethylpolysilanes are also chlorinatively cleaved under similar conditions. Thus, decamethyltetrasilane gave a mixture of 1-chloroheptamethyltrisilane, chloropentamethyldisilane, and chlorotrimethylsilane (approximately 2:1:2).

Table 1. Electron-Transfer Induced Chlorinative Si-Si Bond Cleavage of Dodecamethylcyclohexasilane in CCl_4-CH_2Cl_2 (Conversion and yield are determined by GLC.)

1 (mmol)	**2** (mmol)	CCl_4 (ml)	CH_2Cl_2 (ml)	Time/h	Conversion/%	Yield/%
0.429	0.0657	10.5	4.5	1.0	35	71
0.429	0.0657	10.5	4.5	3.0	54	65
0.502	0.0228	10.0	5.0	3.0	24	78
0.502	0.0482	10.0	5.0	6.0	54	57

From these results, we propose the following scheme as a possible reaction pathway.

$$\begin{array}{llll}
\mathrm{DCA} & & \xrightarrow{h\nu} & \mathrm{DCA^*} \\
\mathrm{DCA^*} & + \ (\mathrm{SiMe_2})_6 & \longrightarrow & \mathrm{DCA}^{\cdot-} + (\mathrm{SiMe_2})_6^{\cdot+} \ (\mathbf{1}^{\cdot+}) \\
\mathbf{1}^{\cdot+} & + \ \mathrm{CCl_4} & \longrightarrow & \mathrm{Me_2Si^+{-}(SiMe_2)_5{-}Cl} \ (\mathbf{4}^+) + \cdot\mathrm{CCl_3} \\
\mathbf{4}^+ & + \ \mathrm{DCA}^{\cdot-} & \longrightarrow & \mathbf{4}\cdot + \mathrm{DCA} \\
\mathbf{4}\cdot & + \ \mathrm{CCl_4} & \longrightarrow & \mathrm{Cl{-}(SiMe_2)_6{-}Cl} \ (\mathbf{3}) + \cdot\mathrm{CCl_3} \\
2\,\cdot\mathrm{CCl_3} & & \longrightarrow & \mathrm{Cl_3CCCl_3}
\end{array}$$

Photooxygenation,8) photoisomerization,9) and photodimerization10) induced by electron-transfer to DCA have been reported recently. The present reaction not only adds another new example of currently interested electron-transfer induced photochemical reactions but provides useful synthetic ways to chlorosilanes.

References

1) Chemistry of Organosilicon Compounds 213.

2) H. Sakurai, K. Sakamoto, and M. Kira, Chem Lett., 1984, 1213.

3) H. Sakurai, M. Kira, and T. Uchida, J. Am. Chem. Soc., 95, 6826 (1973). We have observed CT spectra as well as ESR spectra of tetracyanoethylene anion radicals. See also, H. Watanabe, M. Kato, E. Tabei, K. Yoshizumi, T. Muraoka, Y. Nagai, and T. Sato, XIIth International Conference on Photochemistry, August 1985, Abstracts p.26 (1985).

4) D. Rehm and A. Weller, Isr. J. Chem., 8, 259 (1970).

5) The ΔG value was calculated by using following values: E_{pa} (**1**)=1.45 V,6) $E^{red}_{1/2}$ (DCA)=−0.82 V (SCE), ΔE_{0-0}=68 kcal/mol, $e^2/\varepsilon a$=0.06 eV. The E_{pa} value was used as an approximate oxidation potential of **1**. Details will be reported later.

6) H. Watanabe and Y. Nagai, "Organosilicon and Bioorganosilicon Chemistry, Structure, Bonding, Reactivity and Synthetic Application," H. Sakurai ed., p. 107, Ellis Horwood publishers, Chichester UK (1985).

7) R. A. Barber, P. de Mayo, K. Okada, and S. K. Wong, J. Am. Chem. Soc., 104, 4995 (1982).

8) C. S. Foote, Tetrahedron, 41, 2221 (1985).

9) E. Hasegawa, K. Okada, and T. Mukai, J. Am. Chem. Soc., 106, 6852 (1985).

10) K. Mizuno, H. Kagano, T. Kasuga, and Y. Otuji, Chem. Lett., 1983, 133.

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